

Surface reactions with participation of oxides of molybdenum and tungsten

The kinetics of surface reactions in one-dimensional and radial (two-dimensional) distribution of diffusant MoO_3 (WO_3) on the surface of the substrate MeO (Me is Cd, Ni, Pb, Mn, Cu) were investigated. A kinetic equation satisfactorily describes the rate of surface reactions in the case of radial distribution of diffusant on the substrate. It's found that when the radial distribution of diffusant the growth of layer on the substrate surface eventually slows down and stops almost completely, due to the outflow of the diffusant deeps into the substrate. When the one-dimensional distribution of diffusant the surface interaction is not slowed down and does not stop at an arbitrarily large times.

Keywords: diffusant; molybdates; complex oxides; surface reaction diffusion; scanning electron microscopy (SEM)

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Introduction

The reaction diffusion in the synthesis of molybdates and tungstates, as well as many other complex oxides, includes bulk, grain-boundary and surface diffusion. The separation of these three streams and study of their mechanism is the most important task of the science of solid-phase reactions. In the synthesis of molybdates and tungstates the formation of the reaction product is found not only in the place of contact of the pellets of the reactants, but also outside it, on the surface of one of the reagents (substrate). This indicates a large contribution of surface reaction diffusion (SRD) in a total reaction transfer and provides a unique

opportunity to select and research one of three major streams of the reaction mass.

One of the quantitative characteristics of the SRD is the ratio of the length of the surface layer (ℓ_s) to the thickness of the layer of product at the place of contact of reagents (ℓ). The value of ℓ_s/ℓ for the same diffusants MoO_3 (WO_3) varies in very wide limits from $\ell_s/\ell \approx 1 \dots 180$.

In papers [1–3] more than 20 surface reactions with the participation of MoO_3 (WO_3) were studied and the following basic facts were installed:

1. A sharp slowdown in surface reactions, up to a full stop, after reaching a certain value of the length of the surface layer.

2. The independence of the maximum length of the surface layer ℓ_s^{\max} from the temperature of the experiment; with changes in temperature, only the time to reach ℓ_s^{\max} changes.

3. The dependence of the rate of surface reactions on porosity of the substrate, which is localized on the surface layer. With increasing porosity ℓ_s decreases sharply.

4. The high sensitivity of the speed of SRD to the influence of an electric field; a complex nonmonotonic dependencies ℓ_s (U) are observed.

5. The speed of surface reactions is significantly higher for those reaction pairs where the product of the interaction contains several phases.

Thus, the effect of SRD has been studied well enough. However, the authors [1–3] noted that a number of experimental facts obtained in the study of this phenomenon (for example, termination of surface interaction when reaching a certain value of the length of the surface layer) can not be explained. Further, up

to the present time the research was conducted for this cell geometry, in which the proliferation of diffusant, and, consequently, the growth of the surface layer occurs radially with respect to the place of contact of the reactants. In this case, the diffusion is two-dimensional. At the same time, kinetic dependencies, linking some characteristic speed of the process over time, are obtained for one-dimensional diffusion. In connection with the foregoing, in the present work the following objectives are stated:

1) To obtain the growth equation of the surface layer in the radial distribution of diffusant, which satisfactorily describes the kinetics of surface interactions.

2) To investigate the kinetics of surface interactions in the case of one-dimensional distribution of diffusing into the systems CuO-MoO_3 , $\text{Mn}_2\text{O}_3\text{-MoO}_3$, NiO-MoO_3 , NiO-WO_3 , PbO-MoO_3 .

3) Using scanning electron microscopy (SEM) to study the morphology of the reaction product on the surface and at the site of contact of the reactants.

The experimental part

We used NiO , CuO , MoO_3 , WO_3 , PbO , Mn_2O_3 , CdO (qualification "h.p."). Pb_2MoO_5 was synthesized from simple oxides by standard ceramic technique in three stages with intermediate milling at temperatures of 550–750 °C; time of annealing at each stage was 15 hours. The phase composition was controlled by x-ray. The samples for investigation were prepared in the form of briquettes by pressing and subsequent sintering. The sintering conditions of the samples are given in table 1.

The surface diffusion of the reaction was studied in one-dimensional and two-

dimensional distribution of diffusant. For this purpose we used cells with different geometry of the assembly of briquettes reagents. In one case, the disc diameter of the substrate briquette was 15 mm, and the diameter of the disc diffusant – 5 mm (fig. 1a); in another case substrate had a shape of a bar with a height of 5–10 mm and an area of contact with the surface diffusant 65–75 mm², and the sample diffusant was made in the form of a disk with a diameter of 15 mm and a thickness of 2 mm (fig. 1b). The distribution scheme of diffusant on the substrate is shown by arrows.

Table 1

The sintering conditions of the samples

Compound	Annealing temperature, °C	Annealing time, hour
NiO	1200	6
Mn ₂ O ₃	900	24
Pb ₂ MoO ₅	700	48
PbO	760	24
CuO	950	18
CdO	700	24
MoO ₃	600	3
WO ₃	900	3

Overseeing the development process was carried out by periodic measurement of the length of the surface layer ℓ_s , layer ℓ , formed in the contact area of the briquettes, the weight of the substrate.

X-ray analysis of objects of research was carried out on diffractometer DRF-2.0 in the Co_{K α} radiation. The survey was conducted at a speed of 2 °C/min in the range of angles 2θ from 5 to 35 °C. The interpretation of radiographs was carried out using the card file ASTM.

The microscopic analysis of the surface and chipping of the pellets after annealing was performed using microscope MBS-9 with magnification 16 to 56 times

Results and discussion

The kinetic growth equation of the surface layer in the radial diffusion

As shown earlier [1–3], one interesting feature of the SRD is an atypical form of the kinetic dependences, which have the form of curves with saturation. When analyzing this phenomenon, we drew attention to the fact that a complete shutdown of surface interaction is recorded by conducting experiments for cells with such a geometry assembly of briquettes of re-

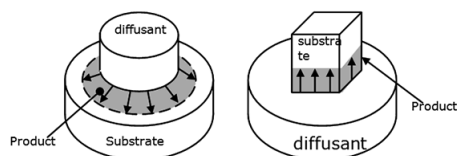


Fig. 1. The scheme of experiments for the investigation of kinetics of surface interactions: *a* – radial distribution of diffusant; *b* – one-dimensional distribution of diffusant.

and optical microscope POLAM S-112 in transmitted light at magnification of 300–420 time.

The morphology of the substrate and product, as well as their elemental composition, was investigated using the electron microscope JSM-3 with a microprobe at magnification of 300–3000 times.

The measurement of the mass of briquettes before and after diffusion annealing was carried out on an analytical balance Sartorius – BL60S with an accuracy of 0.0001 g.

The effective density of samples was determined by the volume and mass of samples and hydrostatic weighing. Its value varied from 60 to 85 %.

gents, which was radial (two-dimensional) distribution of diffusant on the surface of the substrate (fig. 1, *a*).

It are obvious that the classical limit cases for the kinetic and diffusion regimes ($\ell = K\tau$ and $\ell^2 = K\tau$) is not consistent in the description of the kinetics of radial diffusion. When the radial distribution of diffusant, unlike the one-dimensional case, there is a constant increase in the length of the reaction front, which should

lead to change of time dependence of the parameter characterizing the rate of reaction (ℓ_s). Therefore, in this work the task was to obtain a growth equation of the surface layer in the radial distribution of diffusant on the substrate surface.

The derivation of the equation was not taken into account the outflow of diffusant deep into the substrate, i.e. the case of surface reaction diffusion was considered in pure form.

According to the general principles of thermodynamics of nonequilibrium processes the speed of any non-equilibrium process (including chemical reactions) is proportional to some “driving force” of the process and is inversely proportional to a certain effective value of R^* which is the resistance process [4]. The thermodynamic driving force of chemical interaction is the difference in isobaric-isothermal potentials of the reaction ΔG . Then the reaction rate of surface reaction is determined by the ratio:

$$W = \frac{\Delta G}{R^*} \quad (1)$$

On the other hand, the rate of surface reaction can be determined by the area change of a reaction product formed on the surface of the substrate, per unit time, fig. 2.

The rate of surface reaction is determined by varying the amount of reaction product formed on the surface, per unit time:

$$W = \frac{dn_{\text{поб}}}{d\tau} \quad (2)$$

The amount of the substance on the surface is proportional to its volume: $n_{\text{поб}} \sim V_{\text{поб}}$. In turn, the volume of the surface layer is equal to the mathematical product of its area by thickness: $V_{\text{поб}} = S_{\text{поб}} \cdot \delta$. As a first approximation we can assume that

the thickness of the surface of the product (δ) is a constant value, since it is less on orders than the length of the surface layer; then the number of product on the surface is proportional to the occupied of the area: $n_{\text{поб}} \sim S_{\text{поб}}$, which suggests that the reaction rate is equal to the change of the square of the reaction product formed on the surface, per unit time:

$$W = \frac{dS_{\text{поб}}}{d\tau} \quad (3)$$

The resistance of the solid-phase reaction is the sum of resistance of separate stages, the main of which are actually chemical interaction (resistance R_{chem}) and diffusion (resistance R_{dif}):

$$R^* = R_{\text{chem}} + R_{\text{dif}} \quad (4)$$

Equating (1) and (3), we obtain:

$$\frac{dS_{\text{поб}}}{d\tau} = \frac{\Delta G}{R_{\text{хим}} + R_{\text{диф}}} \quad (5)$$

The size of the surface layer is determined by the expression:

$$S_{\text{поб}} = \pi((r + \ell_s)^2 - r^2) = \pi\ell_s(2r + \ell_s), \quad (6)$$

where r – the radius of the briquette diffusant.

It is obvious that the resistance of the chemical stage R_{chem} is proportional to the length of the front surface reactions, i.e. the length of a circle of radius $(r + \ell_s)$:

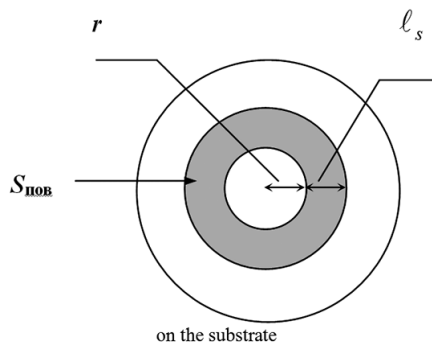


Fig.2. The lay ut of the surface layer (grey colour) on the substrate

$$R_{chem} = a \cdot 2\pi(r + \ell_s), \quad (7)$$

where a is a certain resistivity of the chemical stage, depending on the nature of the reacting substances. The resistance stage of diffusion is directly proportional to the length of the surface layer:

$$R_{dif} = b \cdot \ell_s \quad (8)$$

where b is the resistivity of the diffusion stage. Substituting (6), (7) and (8) into (5), we obtain the expression:

$$\frac{d[\pi\ell_s(2r + \ell_s)]}{d\tau} = \frac{\Delta G}{2\pi a(r + \ell_s)}, \quad (9)$$

which is converted to

$$2\pi \frac{d\ell_s}{d\tau}(r + \ell_s) = \frac{\Delta G}{2\pi a(r + \ell_s) + b\ell_s}. \quad (10)$$

Separating variables and integrating (10), we obtain:

$$4\ell_s \pi^2 a r^2 + \ell_s^2 \pi r(b + 4\pi a) + \frac{2}{3} \ell_s^3 \pi(2\pi a + b) = \Delta G \tau \quad (11)$$

Denoting the constant as follows: $4\pi^2 a r^2 = x$; $\pi r(b + 4\pi a) = y$; $\frac{2}{3}\pi(2\pi a + b) = z$, and substituting in (11), we finally obtain:

$$x\ell_s + y\ell_s^2 + z\ell_s^3 = \Delta G \tau \quad (12)$$

Thus, the dependence of the length of the surface layer with time is described by a polynomial of the third degree.

The derivation of this equation is not stated which of the stages (diffusion or kinetic) limits the entire process. Let us now consider special cases.

Since and R_{chem} , and R_{dif} , according to the equations (7), (8), depend on the length of the surface layer, which increases with time, the resistance of chemical and diffusion stages also will be constantly expanding in the surface reaction. This means that in the case of two-dimensional (radial) diffusion at short times it cannot be neglected diffusion resistance, as in the

one-dimensional case. Then it is obvious that the mode of interaction will depend only on the resistivity which stage (diffusion or kinetic) is larger in magnitude.

Kinetic mode.

When kinetic control of the process the resistivity of the diffusion stage is significantly smaller than the stage of chemical interaction: $b \ll a$, hence $R_{dif} \ll R_{chem}$, that is the diffusion resistance can be neglected.

Then the expression (9) is converted to the following:

$$\frac{d[\pi\ell_s(2r + \ell_s)]}{d\tau} = \frac{\Delta G}{2\pi a(r + \ell_s)}. \quad (13)$$

Making a transformation similar to the above, we get:

$$r^2 \ell_s + r \ell_s^2 + \frac{\ell_s^3}{3} = K_{xhm} \tau, \quad (14)$$

where $K_{xhm} = \frac{\Delta G}{4\pi^2 a}$.

Thus, the dependence of the length of the surface layer from time to time in the case of kinetic control of the process is also described by a polynomial of the third degree.

B) Diffusion regime.

Under the diffusion control of process the resistivity of the diffusion stage is significantly greater than the stage of chemical interaction: $b \gg a$, therefore $R_{dif} \gg R_{chem}$, that is, the resistance stage, the chemical interaction can be neglected. Then the expression (9) is converted to the following:

$$\frac{d[\pi\ell_s(2r + \ell_s)]}{d\tau} = \frac{\Delta G}{b\ell_s}. \quad (15)$$

After transformations we get the equation:

$$r \frac{\ell_s^2}{2} + \frac{\ell_s^3}{3} = K_{\text{нф}} \tau, \quad (16)$$

where $K_{\text{нф}} = \frac{\Delta G}{2\pi b}$.

Thus, when the diffusion control of process the time dependence of the length of the surface layer is described by a third-order polynomial with a zero coefficient for the first member of (ℓ_s).

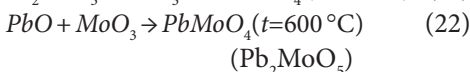
So, when the radial distribution of diffusant on the surface of the substrate the kind of dependence of the length of the surface layer with time is not fundamentally dependent on the interaction mode. In all cases the dependence $\ell_s = f(\tau)$ is described by polynomial of third degree (12).

However, equation (12) does not prescribe a termination surface interaction at sufficiently large times, what was observed experimentally earlier [1–3] for more than a dozen systems studied, as well as in the present work. The reason for the stop of the surface interactions, probably is associated with the outflow of diffusant deep into the substrate that were not considered in the derivation of this equation.

The Investigation of kinetics of surface interaction for radial and one-dimensional distribution of diffusant

As noted previously, the study of the surface reaction diffusion in one-dimensional propagation of diffusant was conducted.

Therefore, in the present work we study the kinetics of surface reactions in the radial and one-dimensional distribution of diffusant (fig. 1) in comparison. The equations of the studied reactions are:
 $\text{NiO} + \text{WO}_3 \rightarrow \text{NiWO}_4 (t=850^\circ\text{C}) \quad (17)$
 $\text{NiO} + \text{MoO}_3 \rightarrow \text{NiMoO}_4 (t=550^\circ\text{C}) \quad (18)$
 $2\text{Mn}_2\text{O}_3 + 4\text{MoO}_3 \rightarrow 4\text{MnMo} + \text{O}_2 (t=600^\circ\text{C}) \quad (19)$



The product Pb_2MoO_5 is in parentheses that can be formed according to the state diagram, but were not detected during this study by means of SRD.

The kinetic dependences of the length of the surface layer by one-dimensional and radial (two-dimensional) diffusion is presented in fig. 3.

From fig. 3 it can be seen that the form of the kinetic curves in one-dimensional and radial (two-dimensional) SRD is different.

In the case of two-dimensional diffusion the curves go out of the saturation quickly (10–20 hours). In order to verify the applicability in the previous section, equation (12) to the description of the kinetics of the SRD in the case of radial diffusion was carried out the processing of the experimental curves 2 (fig. 3) using equation (12), wherein the processing were taken as part of the curve (until saturation). The correlation coefficients are shown in table 2.

Table 2

Correlation coefficients	
System	Correlation coefficients, %
PbO/ MoO ₃	95
Mn ₂ O ₃ /MoO ₃	93
NiO/MoO ₃	96
NiO/WO ₃	92
CdO/MoO ₃	97

High values of correlation coefficients (more than 90 %) show that the equation (12) satisfactorily describes the experimental kinetic data presented in terms of geometry for time that is less than the

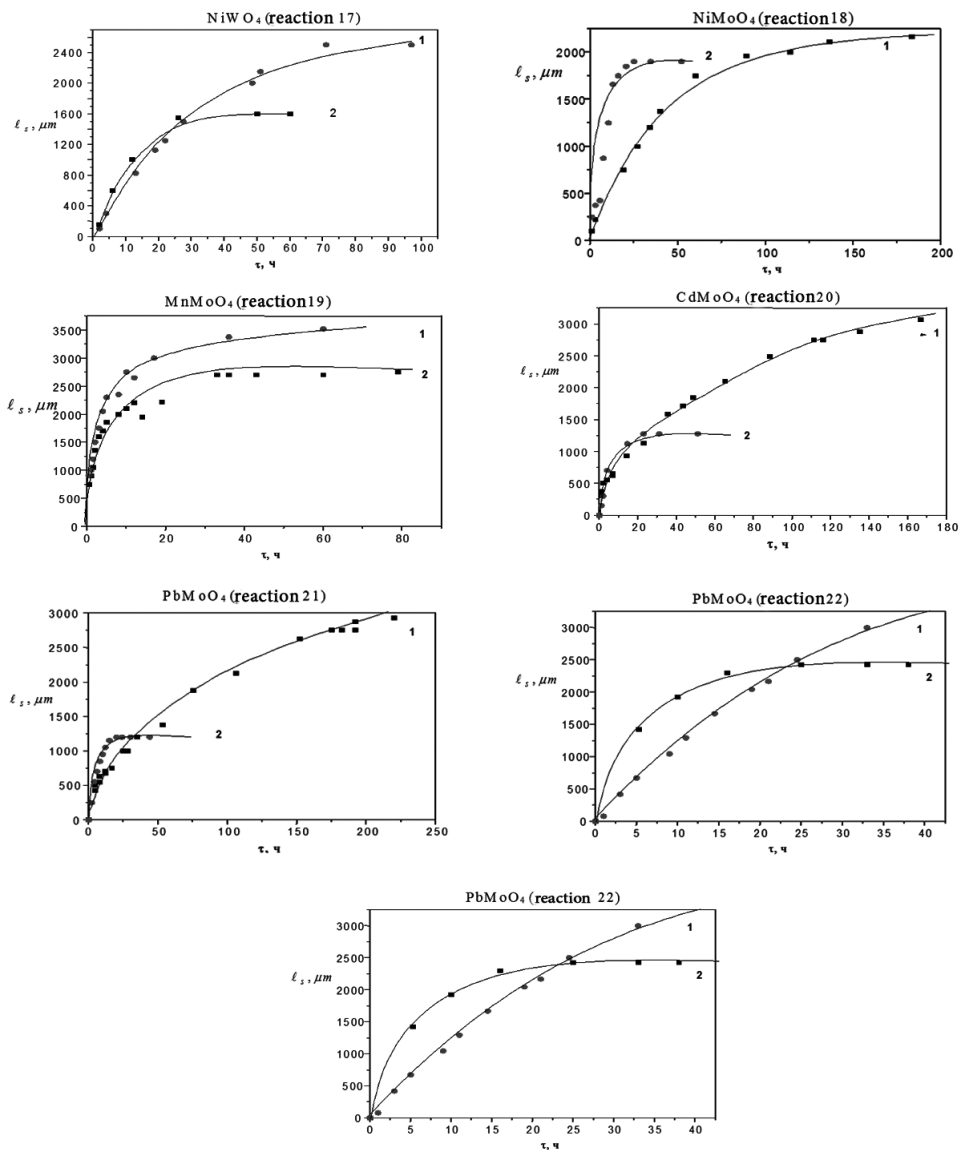


Fig.3. The dependence of the length of the surface layer from time to time:
1 – dimensional; 2 – radial (two-dimensional) distribution of diffusant

critical value τ_{max} at which the maximum value of the length of the surface layer is achieved.

When the one-dimensional distribution of diffusant during annealing over 70–100 hours the change in the length of the surface layer is still so that it is possi-

ble only to ascertain the slowing down at large times, which is reflected in the flattening out of the curve.

At large times (over 100 hours) the boundary between the surface layer of the product and the substrate is very uneven and blurred, so it is very difficult to visu-

ally determine the length of the surface layer. “Blurring” of boundaries, probably associated with the formation of product on the surface not only by surface reactions, but also by gaseous diffusion of MoO_3 . Therefore, the error in determining the length of the surface layer at large times increases.

Therefore, the error in determining the length of the surface layer at large times increases, and using only the method of optical microscopy, it is impossible definitely to determine whether full stop the surface process, or only a sharp slowdown. To solve this problem, we used scanning electron microscopy in combination with x-ray microanalysis.

The value of length of the surface layer in the two-dimensional distribution is always lower than the value in the one-dimensional distribution for the same experiment time.

The reason for this is the fact that when radial diffusion the constant increase is in the length of the three-phase boundary diffusant/substrate/product, which is carried on direct interaction. In the case of one-dimensional diffusion the length of this boundary is constant. That is, the difference of values for two types of geometries is not evidence of differences in the speeds of surface reactions, since in these two cases one- and two-dimensional diffusion is respectively. The relative area occupied by the surface layer (normalized to the contact area of the reactants) $S_{\text{поб}} / S_{\text{конт}}$ is a more correct characterization of the speed of the process, in our opinion. This can be explained by the following considerations. The rate of surface reaction is determined by varying the amount of reaction product formed on the surface, per unit time:

$$W = \frac{dS_{\text{поб}}}{d\tau} \quad (23)$$

The amount of the substance on the surface is proportional to its volume: $n_{\text{поб}} \sim V_{\text{sur}}$. In turn, the volume of the surface layer is equal to the product of its area by thickness: $V_{\text{поб}} = S_{\text{поб}} \cdot \delta$. As a first approximation we can assume that the thickness of the surface of the product (δ) is a constant value, then the amount of surface product is proportional to the occupied area: $n_{\text{поб}} \sim S_{\text{поб}}$, which suggests that the reaction rate is equal to the change of the square of the reaction product formed on the surface, per unit time:

$$W = \frac{dS_{\text{поб}}}{d\tau} \quad (24)$$

In the case of one-dimensional and two-dimensional diffusion the square of the surface layer in different ways depend on ℓ_s . When radial diffusion area of the surface layer is determined by the expression:

$$S_{\text{поб}} = \pi((r + \ell_s)^2 - r^2) = \pi\ell_s(2r + \ell_s), \quad (25)$$

when one-dimensional diffusion is:

$$S_{\text{поб}} = \ell_s \cdot 2(a + b), \quad (26)$$

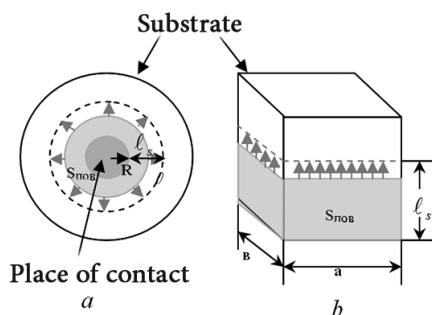


Fig. 4. The scheme of change of the surface area of the reaction product: *a* – radial (two-dimensional) distribution of diffusant; *b* – dimensional distribution of diffusant

where a and b are the length and width of the briquette of the substrate, Fig. 4.

The area of the surface layer depends on the diffusant contact area and the substrate, so it is better to compare not the length, and even not size, and the relative area of the surface layer (i. e., the ratio of the area of the surface layer to the contact area of the reactants). The contact area of the reactants are equal $S_{\text{поб}} = a \cdot b$, where a and b are the sides of the base substrate in the case of one-dimensional diffusion and $S_{\text{кошт}} = 2\pi r^2$, where r is the radius of diffusant, in the case of radial diffusion.

The justice above considerations shows given as an example of the time dependence $S_{\text{поб}} / S_{\text{кошт}}$ for one-dimensional and two-dimensional diffusion in the system Mn_2O_3 - MoO_3 , fig. 5.

Fig. 5 shows that the kinetic dependence $S_{\text{поб}} / S_{\text{кошт}}$ for one-dimensional and two-dimensional distribution of diffusant are close.

Thus, the relative area of the surface layer is a more correct characteristic of the speed of surface reactions: under the radial distribution the diffusant tends to spread out over the surface of the substrate, forming a layer of a shorter length,

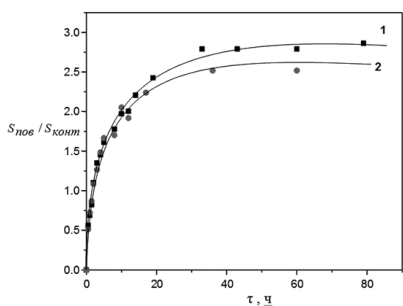


Fig. 5. The dependence of the relative area surface layer to the time the system Mn_2O_3 - MoO_3 : 1 – dimensional, 2 – radial (two-dimensional) diffusion

but approximately the same area as that for one-dimensional diffusion.

To determine the mode of interaction the processing of the kinetic curves was carried out for the case of one-dimensional diffusion equation:

$$\ell^n = K\tau. \quad (27)$$

The values of the coefficient n in equation (27) for the studied systems are shown in table 3.

Table 3

System	coefficient n
CdO/MoO_3	1.94 ± 0.1
NiO/WO_3	1.8 ± 0.1
NiO/MoO_3	1.9 ± 0.1
$\text{Mn}_2\text{O}_3/\text{MoO}_3$	2 ± 0.1
$\text{Pb}_2\text{MoO}_5/\text{MoO}_3$	2 ± 0.1

The coefficient n for all systems is close to 2, therefore, the surface reactions occur in the diffusion mode.

The study of the morphology of the surface layer by electron microscopy

The morphology of the substrate and the layer of product formed as a result of surface reaction diffusion (one-dimensional and two-dimensional) was investigated by electron microscopy with the aim to clarify the following points. First, is it possible to stop the SRD when one-dimensional diffusion, or diffusion on the substrate surface does not stop until the source diffusion is not exhausted. For this purpose, in addition to REM, also x-ray microanalysis of sample was conducted.

Secondly, does the morphology of the product layer at the site of contact of the pellets of the reactants differ on the morphology of the surface layer?

REM-studies were conducted for six systems: $\text{CdO}-\text{MoO}_3$, $\text{CuO}-\text{MoO}_3$, $\text{PbO}-$

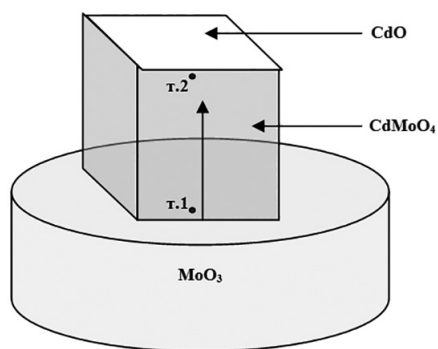
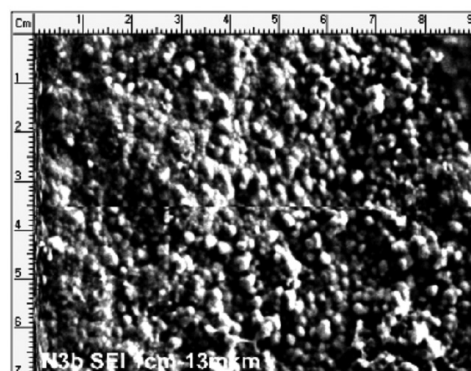


Fig.6. Scheme of direction SEM-photography of the sample

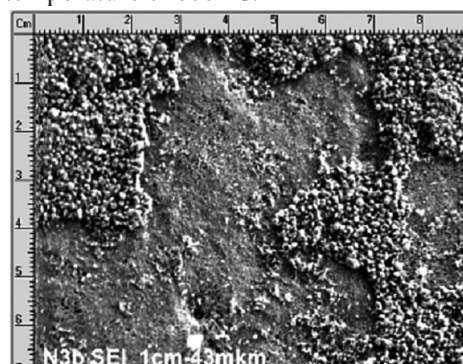
MoO_3 , NiO-MoO_3 , NiO-WO_3 , $\text{Mn}_2\text{O}_3\text{-MoO}_3$. As an example, the results of REM studies of one-dimensional diffusion in the system CdO-MoO_3 and radial (two-dimensional) diffusion in the system NiO-MoO_3 are given.

The System CdO-MoO_3

The sample for the survey was obtained by means of contact diffusion couple annealing the pellets at the propagation of one-dimensional diffusing into the for 167 hours at a temperature of 550 °C. Shooting direction is shown by the arrow from point 1 to point 2, Fig. 6.



a



b

Fig.7. The PEM image of the surface layer of the product CdMoO_4 on the substrate CdO :
 a – in point 1, $\times 1000$; b – in point 2, $\times 300$ (Fig. 6).

REM-images of the product CdMoO_4 in point 1 and 2 (Fig. 6) are shown in Fig. 7 a, b. The grain product have an average size of 4–5 μm (Fig. 7a). When moving off from the contact points, the layer acquires a loose structure, sometimes peels off from the substrate (Fig. 7 b).

In place of the detachment of the product the fine grains of the substrate CdO size 1 - 2 μm are visible. Product CdMoO_4 completely covers the substrate CdO , as evidenced by both REM-images and x-ray microanalysis data, which show the presence of molybdenum on the entire surface of the sample (Fig. 8).

Thus the conclusion made earlier is confirmed that in one-dimensional propagation of diffusant the growth of the surface layer does not stop at an arbitrarily large times, until the source diffusion is exhausted.

The System NiO-MoO_3

The sample for the survey was obtained by means of contact diffusion couple annealing the pellets at the radial distribution of diffusant into the 4 hours at a temperature of 600 °C.

The shooting direction is shown by the arrow (Fig. 9).

Analysis of REM-images shows that the grain size of the product NiMoO_4 is approximately the same at all points of the sample and 1–2 μm , fig. 10.

As mentioned earlier, it is impossible to determine the length of the surface layer by the method of optical microscopy. For more accurate determination by x-ray microanalysis the concentration profile [Mo] and [Ni] was withdrawn, fig. 11.

The graph shows that the concentration of Mo in place of the contact of the briquettes of diffusant/substrate is high and constant

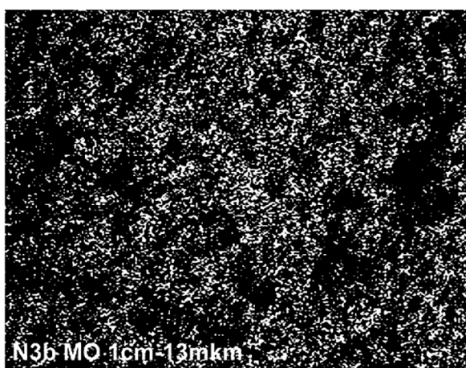


Fig. 8. The distribution of x-ray density of molybdenum on the surface of the substrate at a distance of 4.5 cm from the contact

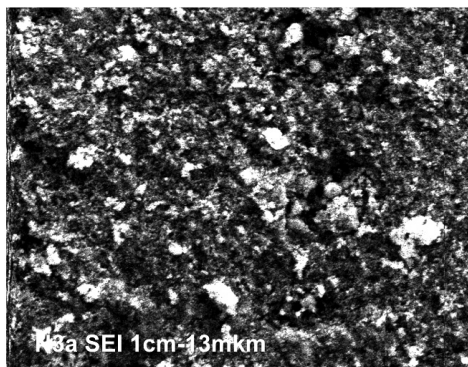


Fig. 10. The PEM image of the surface layer of the product NiMoO_4

on size then as the distance from the contact is sharply reduced. This is due to the radial spread of diffusant on the surface of the substrate wherein the length of the reaction boundary is constantly growing whereby the front edge of the diffusion formation of a continuous layer of a product is not happened the product grains are alternated with the grains substrate, which physically corresponds to the descending order of the concentration of molybdenum as diffusant. Product grains are alternated with the substrate, which physically corresponds to the descending order of the concentration of molybdenum as diffusant.

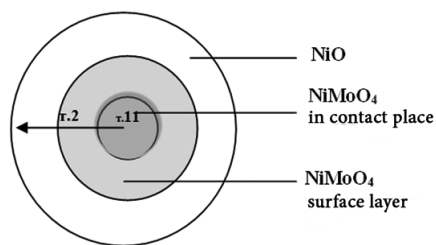


Fig. 9. Scheme of direction SEM-photography of the sample

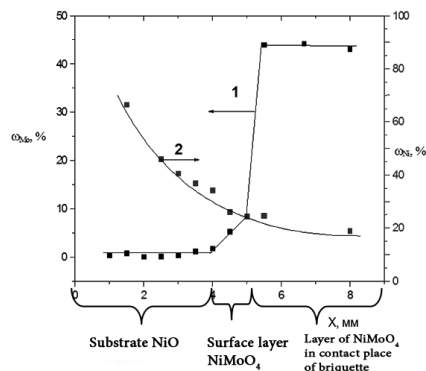


Fig. 11. Concentration profile (1) Mo; (2) Ni in the NiO sample with a layer of NiMoO_4 (x-ray microanalysis data)

The spot on the sample, where the fixed sharp decrease in the concentration of molybdenum is fixed, coincides with

the length of the surface layer, determined by optical microscopy (1200 μm).

Similar results are obtained for the other investigated systems.

Conclusions

The results of this work we can draw the following conclusions:

1. The resulting equation of growth of the surface layer in the radial distribution of diffusant satisfactorily describes the kinetics of surface interactions at times that are lower than the terminating surface reactions.

2. The kinetics of surface interactions in the case of one-dimensional distribution of diffusant is investigated. It is established that surface reactions occur in the diffusion mode and unlike radial diffusion surface interaction does not stop even at large times.

3. It is found that the length of the surface layer in one-dimensional diffusion is greater than when radial and the relative area occupied by the surface product is almost the same in both cases. The latter testifies to the same speed of surface reactions in the radial and one-dimensional distribution of diffusant.

4. The morphology of the substrate surface layer and the morphology of the product formed at the site of contact of the briquettes was investigated. It is established that the surface layer on the front lines of reaction diffusion is not continuous but consists of individual grains.

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